PATENT ABSTRACTS OF JAPAN

(11)Publication number : 08-091857

(43)Date of publication of application : 09.04.1996

(51)Int.Cl. C03B 20/00
C03B 27/012

(21)Application number : 06-229263

(22)Date of filing : 26.09.1994

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(54) ANNEALING METHOD OF SILICA GLASS

(57)Abstract:

PURPOSE: To obtain a annealing method of a silica glass, which is capable of producing a high homogeneous silica glass lump small in strain in high yield.

CONSTITUTION: The annealing method of the silica glass is for annealing the silica glass covered with a vessel, powder or board. The vessel, powder or board consists preferably of silica. And the vessel, powder or board consists of a material having ≥0.004 to <0.08 (cal.s-1.cm-1.°C-1) thermal conductivity.

LEGAL STATUS

[Date of request for examination] 31.07.2001

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

* NOTICES *

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the annealing approach which heat-treats by putting silica glass into a container, embedding to powder, or carrying out surrounding with a plate etc. in detail about the annealing approach for obtaining the high silica glass of whenever [homogeneity].
[0002]
[Description of the Prior Art] In recent years, a silica glass pair is carried out and the demand of the improvement in many physical properties is increasing increasingly. Especially about the homogeneity which is one of the fundamental physical properties of glass, improvement in a property is demanded strongly. The application of silica glass is various, and although it is optical applications, such as prism and a lens, that homogeneity is required, homogeneity with the especially high cube corner reflector (cube-corner prism) carried in the lens used for the excimer laser stepper used for semi-conductor manufacture especially, a satellite, etc. is demanded.
[0003] Conventionally, first, the silica glass for optics selects a good part out of a glass ingot, and starts the ** material of the size doubled with the object made into the purpose from this part. Subsequently, heating maintenance of this ** material is carried out for dozens of days from several hours at temperature a little higher than the temperature defined as a slowly cooling point, it exists in the interior of glass, and distortion which worsens homogeneity is removed. Then, the method of giving and obtaining annealing of occasionally cooling over the long time amount of several months from dozens of hours, to temperature a little lower than the temperature defined as a point [strain], so that distortion by cooling may not newly enter was common.
[0004] However, even if it applied for a long time and gave annealing like the above, distortion was observed near the front face of ** material, and the phenomenon in which homogeneity got worse in this part was often observed. This is for a temperature gradient to arise in a part for a glass lump's surface part, and a core, and for distortion to occur near the front face from the difference of thermal expansion in a cooling process. Therefore, allowances must be given to the dimension to need and the approach of annealing larger ** material must be taken so that the part may be avoided even if it performs cooling on which still longer time amount was spent or distortion remains near a front face so that distortion may not go into a surface part, when it is going to obtain a homogeneous high glass lump, that is, the existing distorted part can be removed and used.
[0005] Even if it takes which approach, in order to obtain a high homogeneity glass lump, long duration was required, a throughput is bad or there was a problem that the product yield will fall.
[0006]
[Problem(s) to be Solved by the Invention] The purpose of this invention is to offer the annealing approach that it is a short time and a homogeneous high silica glass lump can be obtained with the sufficient yield.
[0007]
[Means for Solving the Problem] In order to solve the above-mentioned technical problem, as a result of

inquiring wholeheartedly, in order for this invention persons to give annealing, without leaving distortion to a silica glass lump's front face If a silica glass lump is covered by a silica or the quality of a silica, for example, a silica-alumina system oxide, and the matter by which thermal conductivity does not differ from a silica greatly and a substantial front face is made on a glass lump's outside It comes to complete a header and this invention for distortion going into the part of a cover and not going into a silica glass lump.

[0008] That is, the annealing approach offered by this invention has the description of putting a silica glass lump into the container which consists of a silica etc., embedding to powder, or carrying out whether it surrounding with a plate, or it inserting, and performing annealing treatment, in order to give a silica glass lump the above conditions.

[0009]

[Function] Hereafter, this invention is explained to a detail.

[0010] The description of this invention offers the annealing approach for obtaining a homogeneous high silica glass lump with the sufficient yield for a short time. Homogeneity's being high in glass is in addition to there being no mixing of a bubble or a foreign matter, there being no bias in a presentation, and there being no local fluctuation part of the refractive index represented by the stria, not existing, if [fixed] there is mechanical / thermal distortion at all. Height homogeneous by how generally a thing called high homogeneity glass has little distortion to which it is a premise to which that there are no heterogeneity parts, such as a bubble, a foreign matter, a bias of a presentation, and a stria, and it exists in glass is decided.

[0011] Therefore, the stress relief actuation by annealing is very important actuation for obtaining homogeneous high glass. annealing was described previously -- as -- a glass lump -- ****** (temperature from which the viscosity of the glass serves as eta= 12.0/Pa-s of log(s)) -- number - dozens of degrees C and a case -- 100-degree-C order and high temperature -- a temperature up -- carrying out the temperature -- fixed time amount maintenance -- carrying out -- subsequently -- the temperature to a point [strain] (temperature from which this viscosity serves as eta= 13.5/Pa-s of log(s)) -- number - they are dozens of degrees C and the actuation with main cooling slowly even to low temperature around 100 degrees C depending on the case.

[0012] In here, each temperature, and the holding time and a cooling rate are decided by a presentation and magnitude of glass. If a cooling rate is too quick in the case of annealing, the difference of temperature will arise in a part for a surface part and a core. Then, a surface part precedes contraction accompanying cooling. This becomes a cause and distortion occurs near [large] the glass front face of especially a temperature gradient. Distortion which exists in glass serves as a cause which spoils the homogeneity of the glass. Therefore, at the time of cooling after heating, the annealing actuation for raising the homogeneity of glass is the cooling rate carried out very slowly, and is performed by spending long duration so that the temperature gradient more than [which it is between a part for a core and a surface part] fixed may not arise. However, if a glass lump's magnitude becomes large more than fixed, it will become difficult to store the temperature gradient of the core at the time of cooling and a front face in tolerance, and distortion will occur in a part for a periphery for the reason explained previously. Generally, the existing distorted part cannot be used as high homogeneity glass, but grinding etc. cannot but remove it.

[0013] Therefore, if distorted generating in this surface part can be prevented, the yield of high homogeneity glass and productivity will improve by leaps and bounds. The annealing approach of this invention covers a glass lump's front face with a container, powder, or a plate etc. which consists of a silica etc., and performs heating and cooling processing. Considering a glass lump as wrap matter, a silica is desirable. Moreover, even if it is except a silica, in the highest temperature in annealing actuation, it exists in stability, and it does not react with silica glass, and the thermal conductivity in 100 degrees C should just be or more 0.004 the matter which is less than 0.080 (cal-s-1, cm-1, and **-1). According to this approach, periphery parts, such as a wrap container, serve as a front face in a silica glass lump, and a glass lump's front face is no longer a substantial front face. Therefore, near a glass lump's front face, it becomes large [the temperature gradient at the time of cooling] on front faces, such

as a container, with a loose thing, and a deformation amount will also enter in a tolerance limit. thus, according to the annealing approach of this invention, compared with the former, a yield and productivity can be boiled markedly, and high homogeneity glass can be manufactured well.
[0014]
[Example] The following examples explain this invention in more detail.
[0015] In addition, the homogeneous evaluation approach is as follows. Change produces the part which distortion generated in a refractive index. Then, homogeneous measurement was carried out by measuring refractive-index distribution (deltan). In here, it will be said that homogeneity is good, so that a service area is large, if delta n value is so the same that the width of face (delta n value) of refractive-index distribution is small. The Fizeau interferometer was used for the detailed survey of refractive-index distribution.
[0016] It built example 1, the silica glass lump whose x horizontal x height is 100mmx100mmx100mm was put into the container with which ** 200mmx200mmx200mm and inside dimension consist of silica glass which is abbreviation 100mmx100mmx100mm outside, and it set to the muffle furnace. The temperature up of the inside of a furnace was carried out at 100 degrees C/hour in rate from a room temperature to 1230 degrees C in the atmospheric-air ambient atmosphere, it held at 1230 degrees C for 7 hours, the temperature was continuously lowered the temperature and lowered at 90 degrees C/hour in rate to 900 degrees C by 48 degrees C/hour in rate to 1000 degrees C, and to 660 more degrees C, the temperature was lowered in 240 degrees C /in an hour, and furnace cooling was carried out after that.
[0017] When refractive-index distribution of a glass lump cooled to the room temperature was measured, it was deltan=2.0x10-6 in service area 100mmx100mm.
[0018] the silica glass lump of example 2 example 1 and the same size -- outside -- ** 200mmx200mmx200mm and inside dimension -- about 180 -- the bottom of the container which consists of silica glass which is mmx180mmx180mm was covered with quartz sand (mean particle diameter of about 1mm) at the thickness of 40mm -- it put in in the center mostly, and it was further alike, the clearance between containers was filled up with quartz sand even at the container topmost part, and it covered, and set to the muffle furnace. In the atmospheric-air ambient atmosphere, the temperature up was carried out at 100 degrees C/hour in rate from a room temperature to 1230 degrees C, it held at 1230 degrees C for 7 hours, and the temperature was continuously lowered the temperature and lowered at 90 degrees C/hour in rate to 900 degrees C by 48 degrees C/hour in rate to 1000 degrees C, and to 660 more degrees C, the inside of a furnace was lowered in 240 degrees C /in an hour, and carried out furnace cooling after that.
[0019] When refractive-index distribution of a glass lump cooled to the room temperature was measured, it was deltan=2.0x10-6 in deltan=2.6x10-6,100mmx90mm at service area 100mmx100mm.
[0020] The silica glass lump of example of comparison 1 example 1 and the same size was set to the muffle furnace. The temperature up was carried out at 100 degrees C/hour in rate from a room temperature to 1230 degrees C, and it held at 1230 degrees C for 7 hours, the temperature was continuously lowered the temperature and lowered at 90 degrees C/hour in rate to 900 degrees C by 48 degrees C/hour in rate to 1000 degrees C, and to 660 more degrees C, the inside of a furnace was lowered in 240 degrees C /in an hour, and carried out furnace cooling after that. The furnace atmosphere was made into the atmospheric-air ambient atmosphere from beginning to end.
[0021] When refractive-index distribution of a glass lump cooled to the room temperature was measured, it was deltan=2.0x10-6 in deltan=9.8x10-6 and 50mmx50mm at service area 100mmx100mm.
[0022] The silica glass plate of example 3 size 160mmphix100mmt was inserted from the upper and lower sides with two silica glass plates of 160mmphix50mmt, and was set to the muffle furnace. The temperature up was carried out at 100 degrees C/hour in rate from a room temperature to 1230 degrees C, and it held at 1230 degrees C for 7 hours, and lowers the temperature and continued [lowered the temperature and] at 90 degrees C/hour in rate to 900 degrees C continuously by 48 degrees C/hour in rate to 1000 degrees C, and to 660 degrees C, the inside of a furnace was lowered in 240 degrees C /in an hour, and carried out furnace cooling after that. The furnace atmosphere was made into the

atmospheric-air ambient atmosphere from beginning to end. When refractive-index distribution of a glass lump cooled to the room temperature was measured, it was deltan=2.0x10-6 in deltan=3.0x10-6,150mmphi at 160mm of service areas phi.

[0023] the silica glass plate of example 4 example 3 and the same size -- outside -- ** 200mmx200mmx200mm and inside dimension -- about 180 -- the bottom of the container which consists of silica glass which is mmx180mmx180mm was covered with quartz sand (mean particle diameter of about 1mm) at the thickness of about 65mm -- it put in in the center mostly, and it was further alike, the clearance between containers was filled up with quartz sand even at the container topmost part, and it covered, and set to the muffle furnace. The temperature up was carried out at 100 degrees C/hour in rate from a room temperature to 1230 degrees C, and it held at 1230 degrees C for 7 hours, the temperature was continuously lowered the temperature and lowered at 90 degrees C/hour in rate to 900 degrees C by 48 degrees C/hour in rate to 1000 degrees C, and to 660 more degrees C, the inside of a furnace was lowered in 240 degrees C /in an hour, and carried out furnace cooling after that. The furnace atmosphere was made into the atmospheric-air ambient atmosphere from beginning to end. When refractive-index distribution of a glass lump cooled to the room temperature was measured, it was deltan=2.0x10-6 in 160mm of service areas phi.